Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


**Supplementary Information**

# Study of the interactions between Brønsted acids and triethylphosphine oxide in solution by $^{31}$P NMR: evidences for 2:1 species

Elisabet Pires and José M. Fraile*

*Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Facultad de Ciencias, CSIC-Universidad de Zaragoza, Pedro Cerbuna 12, E-50009 Zaragoza, Spain*

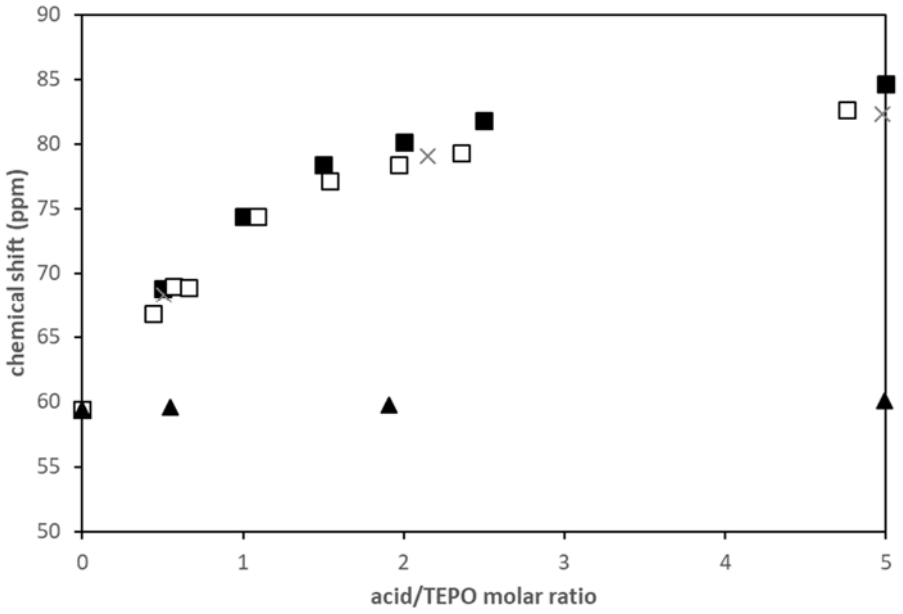


Figure S1. Variation of $^{31}$P chemical shift (ppm) with the acid/TEPO molar ratio in MeOH-$d_4$: (▲) $PhPO_3H_2$, (□) $MeSO_3H$, (×) *p*TosOH, (■) TfOH.

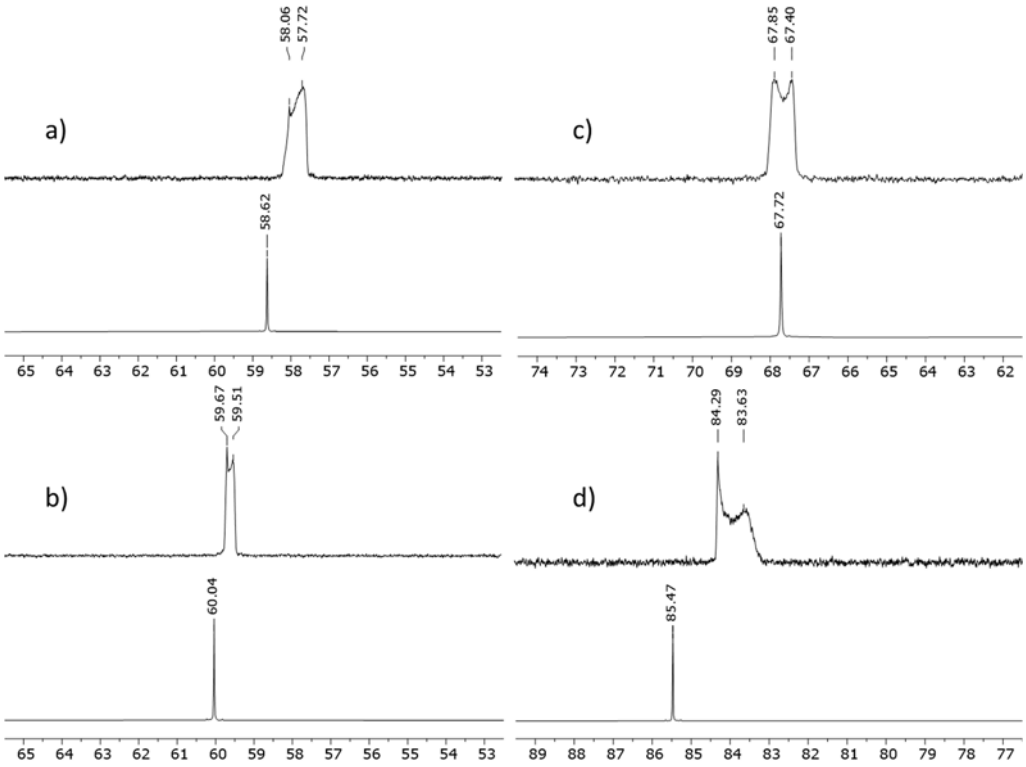


Figure S2. $^{31}$P NMR spectra of acid-TEPO mixtures in $CDCl_3$ at short (top) and long (bottom) equilibration time with different nominal molar ratios: a) AcOH/TEPO = 5; b) AcOH/TEPO = 15; c) TFA/TEPO = 2.5; d) $MeSO_3H$/TEPO = 5.


**Fig. S3.** Variation of $^{31}P$ chemical shift (ppm) with TFE/TEPO molar ratio in $CDCl_3$.

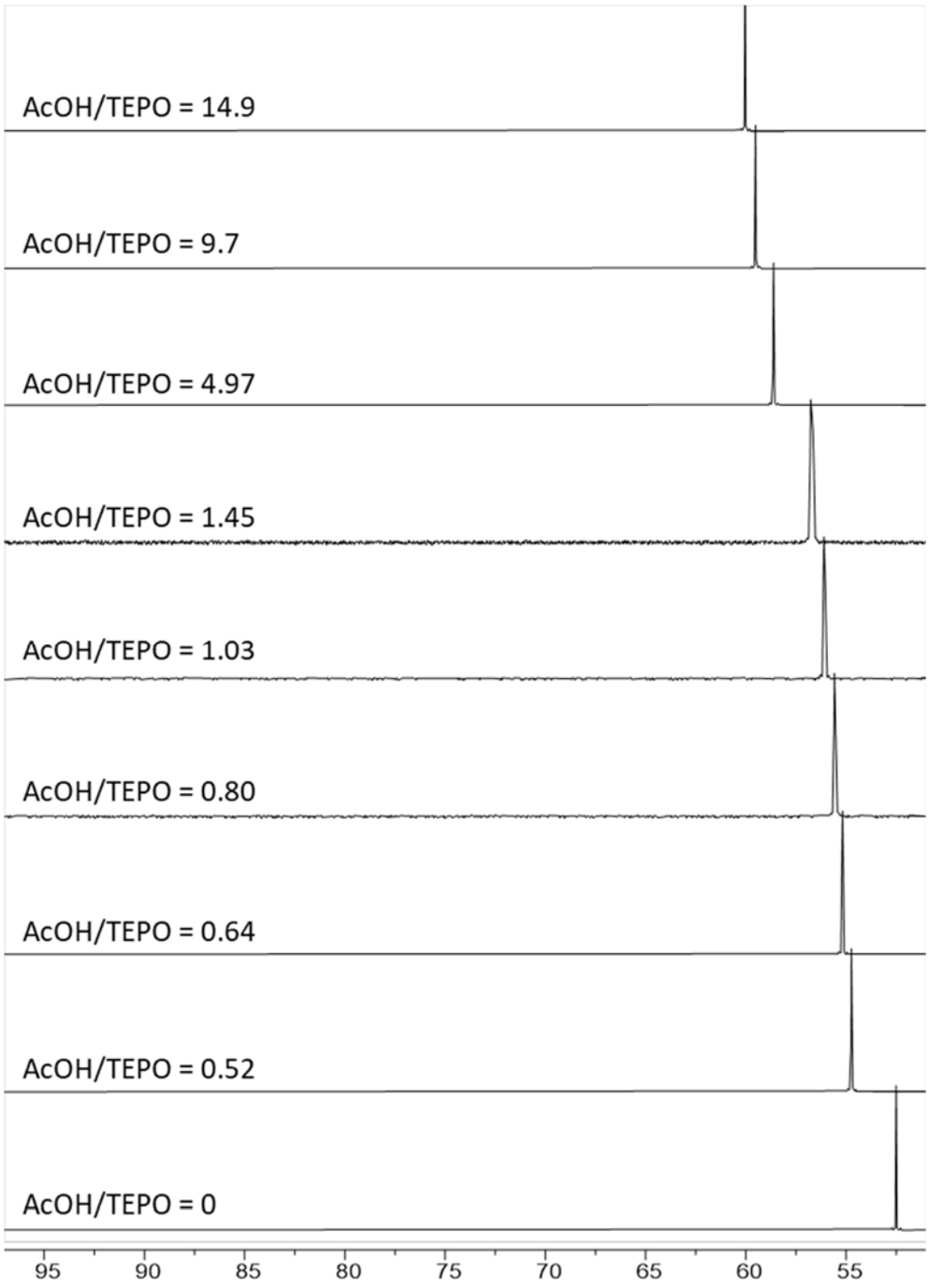


**Fig. S4.** Variation of $^{31}P$ chemical shift (ppm) with AcOH/TEPO molar ratio in $CDCl_3$.

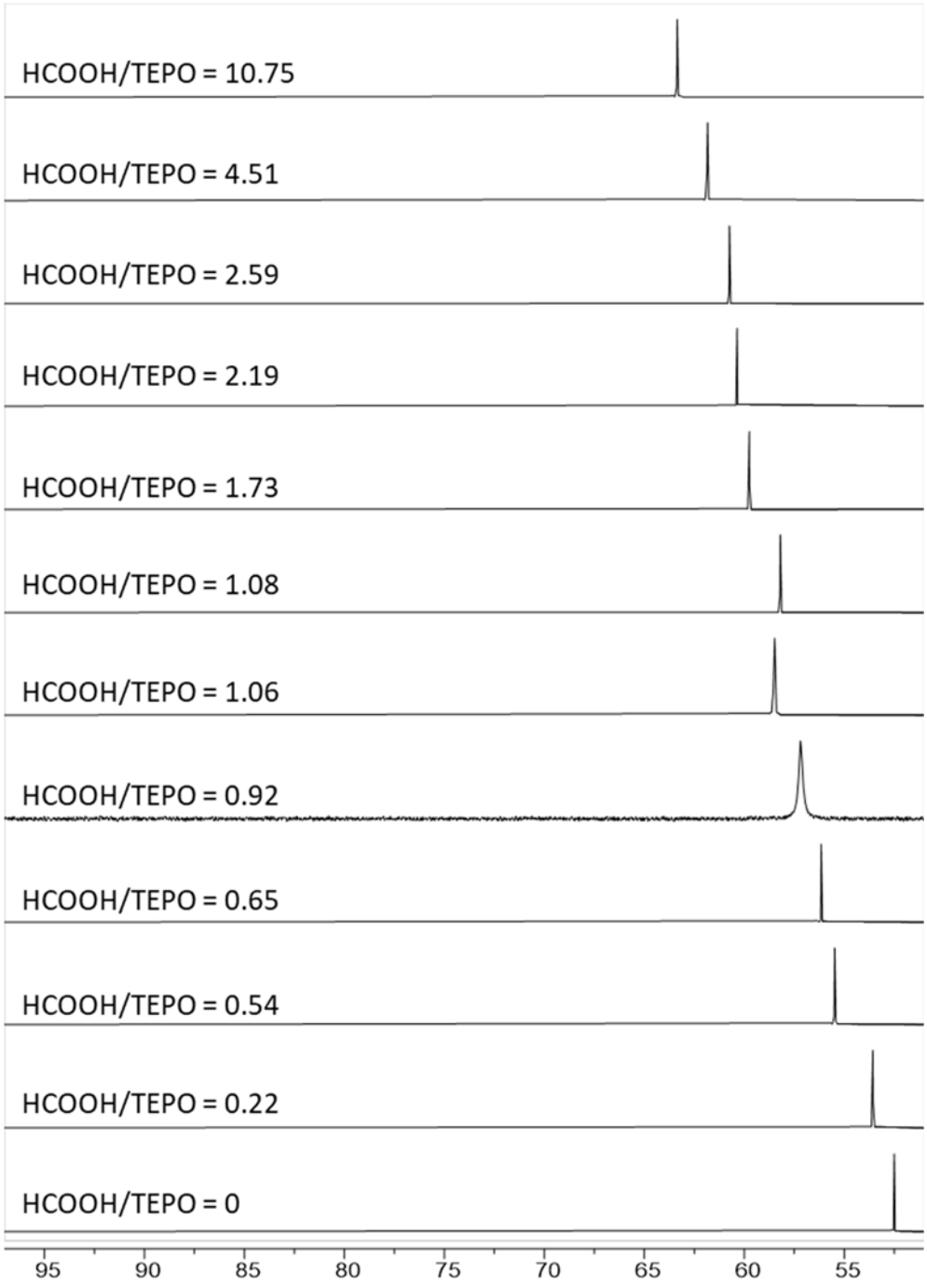


**Fig. S5.** Variation of $^{31}P$ chemical shift (ppm) with HCOOH/TEPO molar ratio in $CDCl_3$.

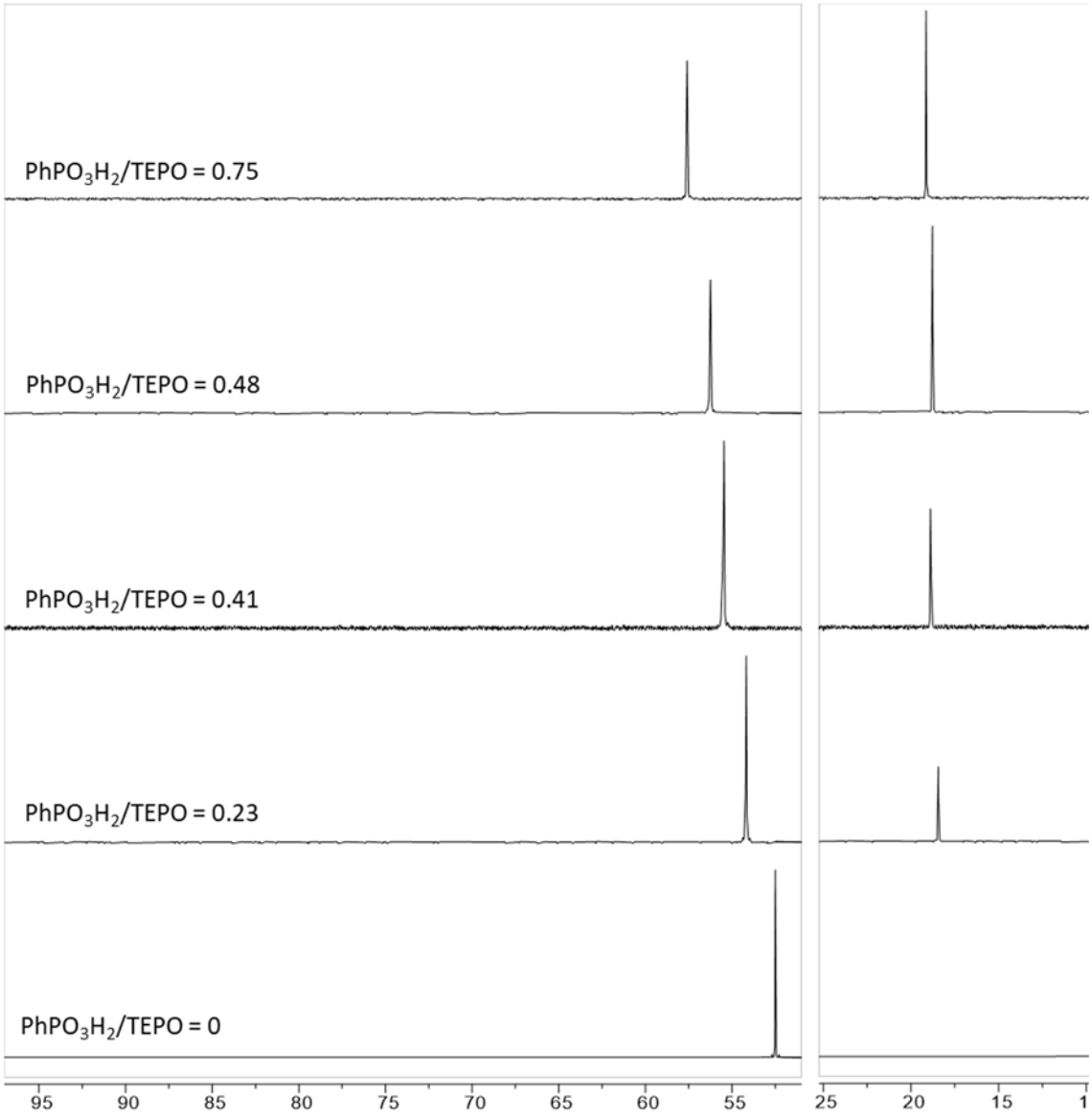


**Fig. S6.** Variation of $^{31}P$ chemical shift (ppm) with $PhPO_3H_2$/TEPO molar ratio in $CDCl_3$. On the right (≈ 19 ppm), the signal corresponding to $PhPO_3H_2$.

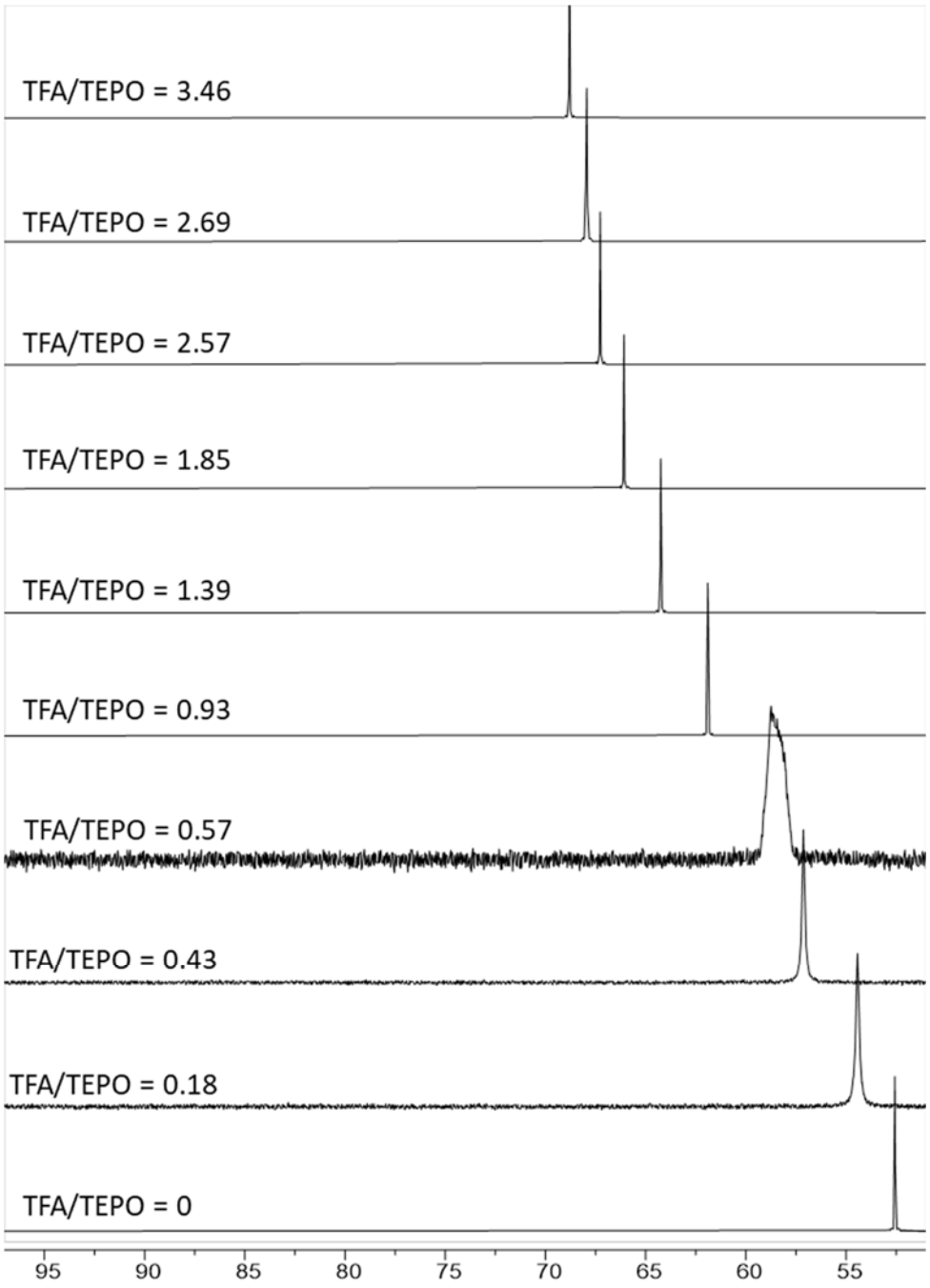


**Fig. S7.** Variation of $^{31}P$ chemical shift (ppm) with TFA/TEPO molar ratio in $CDCl_3$.

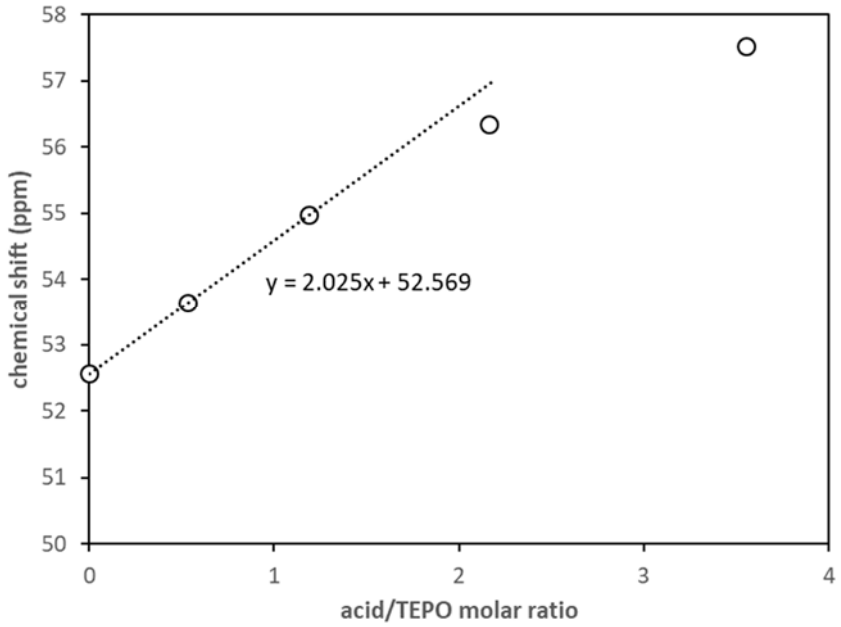


**Fig. S8.** Linear fit of $^{31}$P chemical shift (ppm) at low TFE/TEPO molar ratio.

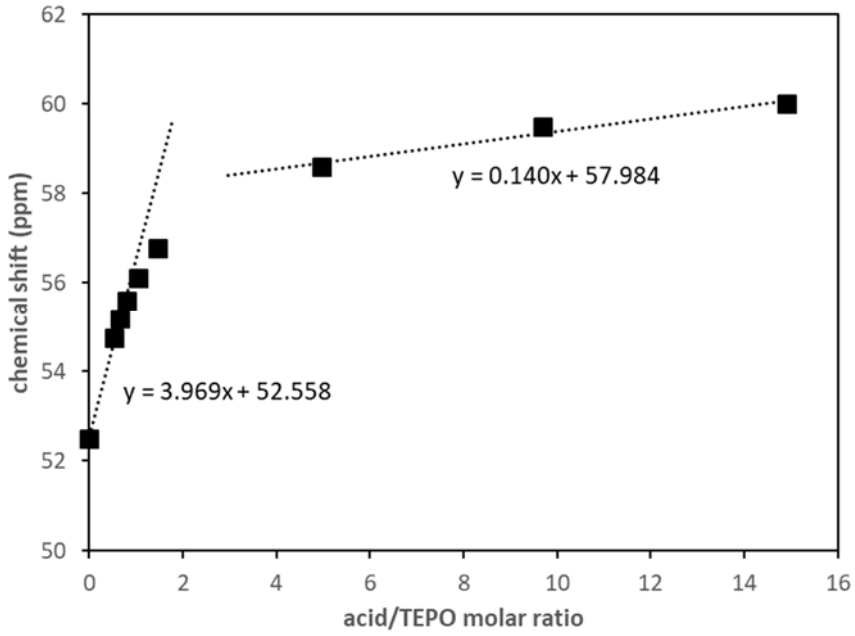


**Fig. S9.** Linear fits of $^{31}$P chemical shift (ppm) at low and high AcOH/TEPO molar ratios.

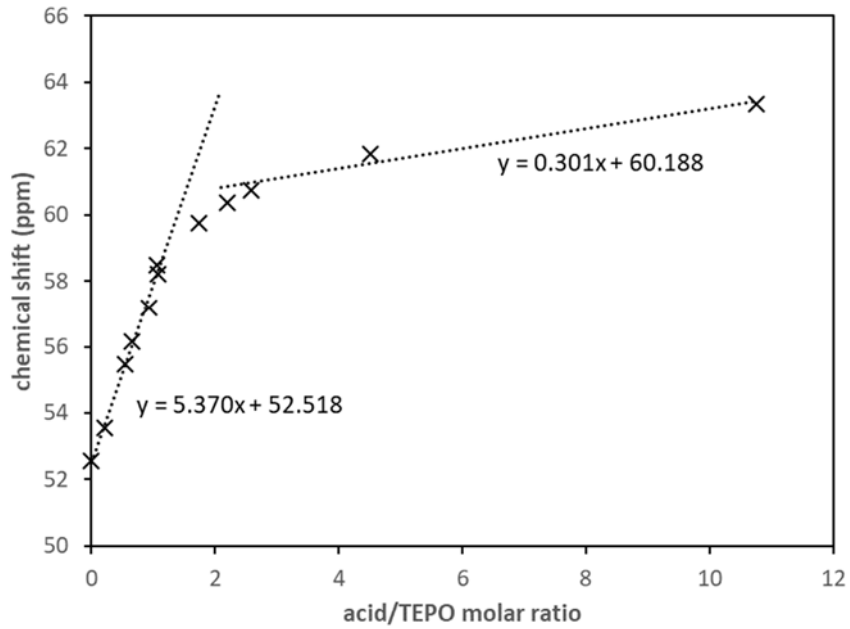


**Fig. S10.** Linear fits of $^{31}$P chemical shift (ppm) at low and high HCOOH/TEPO molar ratios.

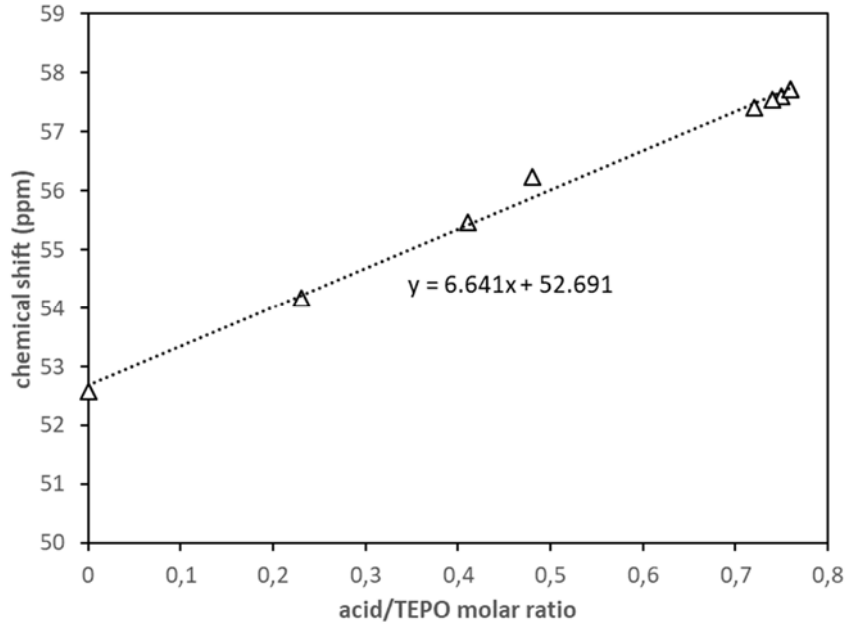


**Fig. S11.** Linear fit of $^{31}$P chemical shift (ppm) at low $PhPO_3H_2$/TEPO molar ratio.

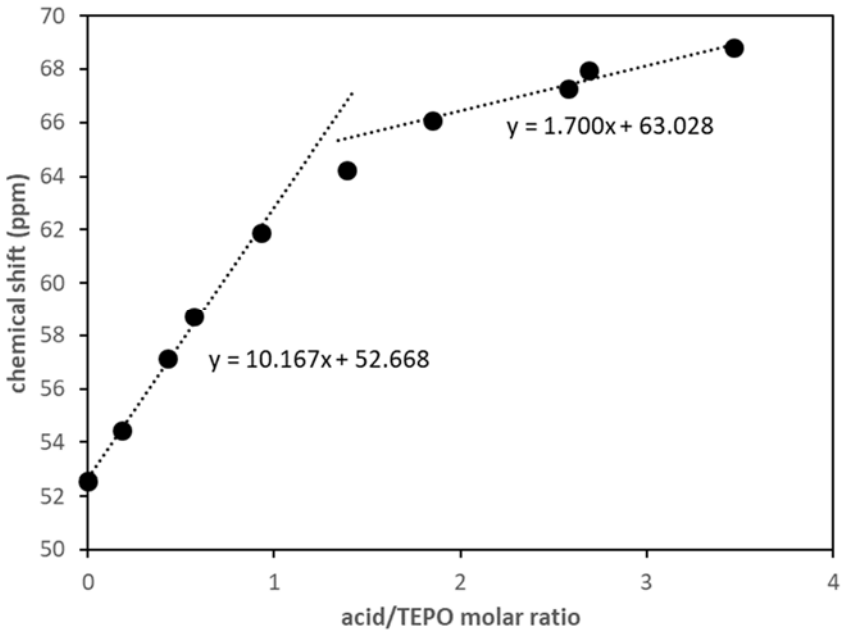


**Fig. S12.** Linear fits of $^{31}$P chemical shift (ppm) at low and high TFA/TEPO molar ratios.

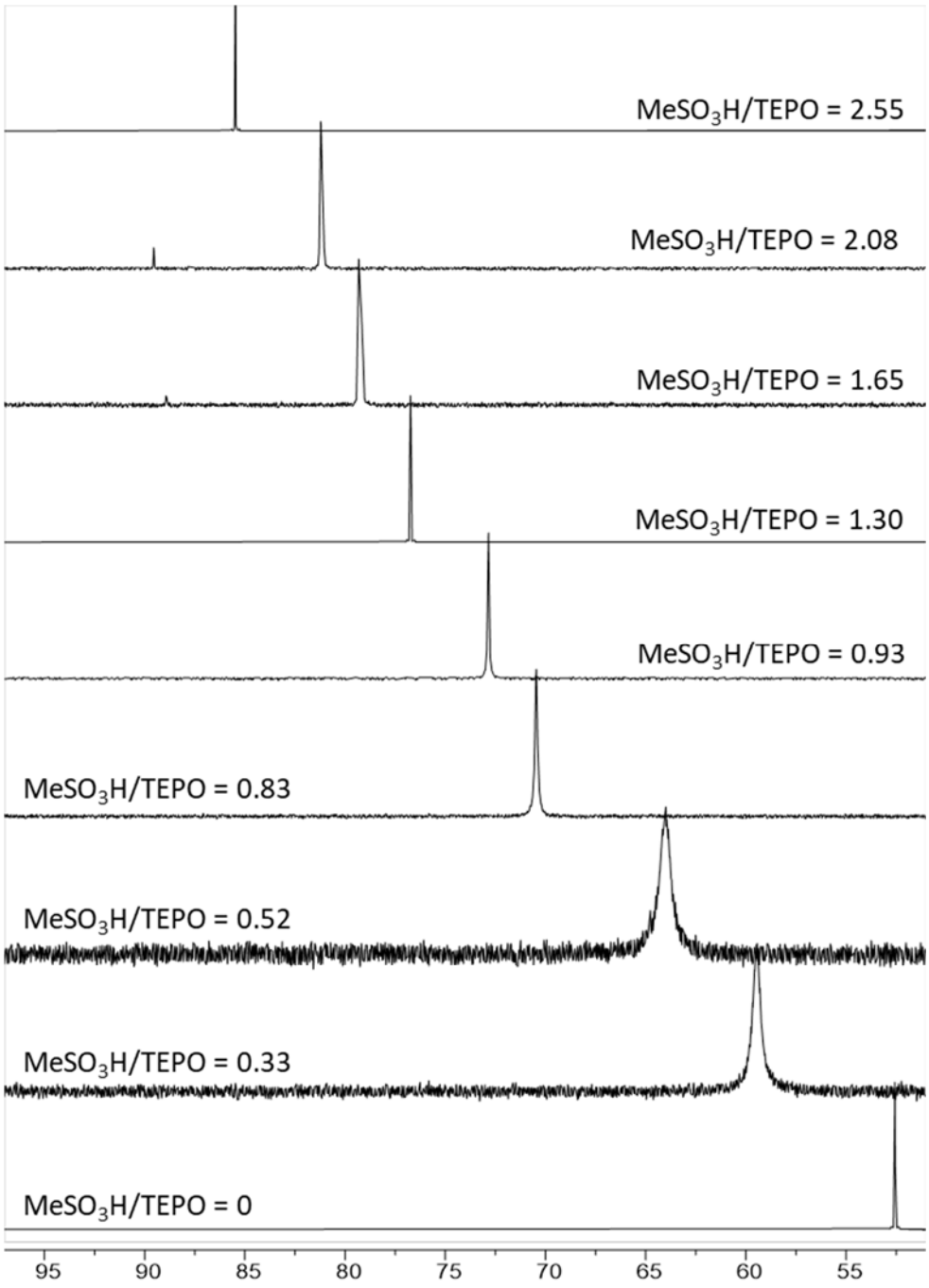


**Fig. S13.** Variation of $^{31}P$ chemical shift (ppm) with $MeSO_3H$/TEPO molar ratio in $CDCl_3$.

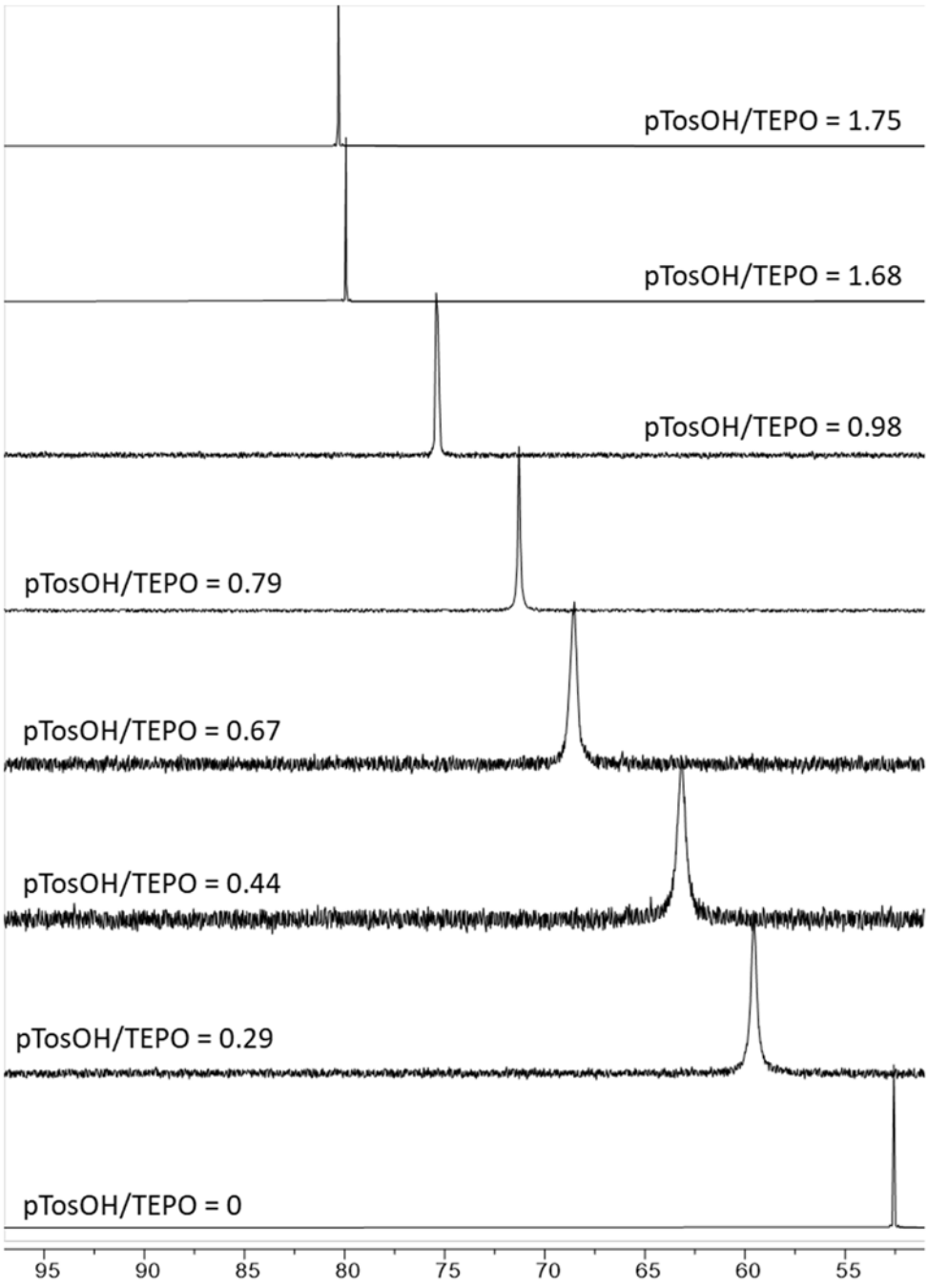


**Fig. S14.** Variation of $^{31}P$ chemical shift (ppm) with pTosH/TEPO molar ratio in $CDCl_3$.

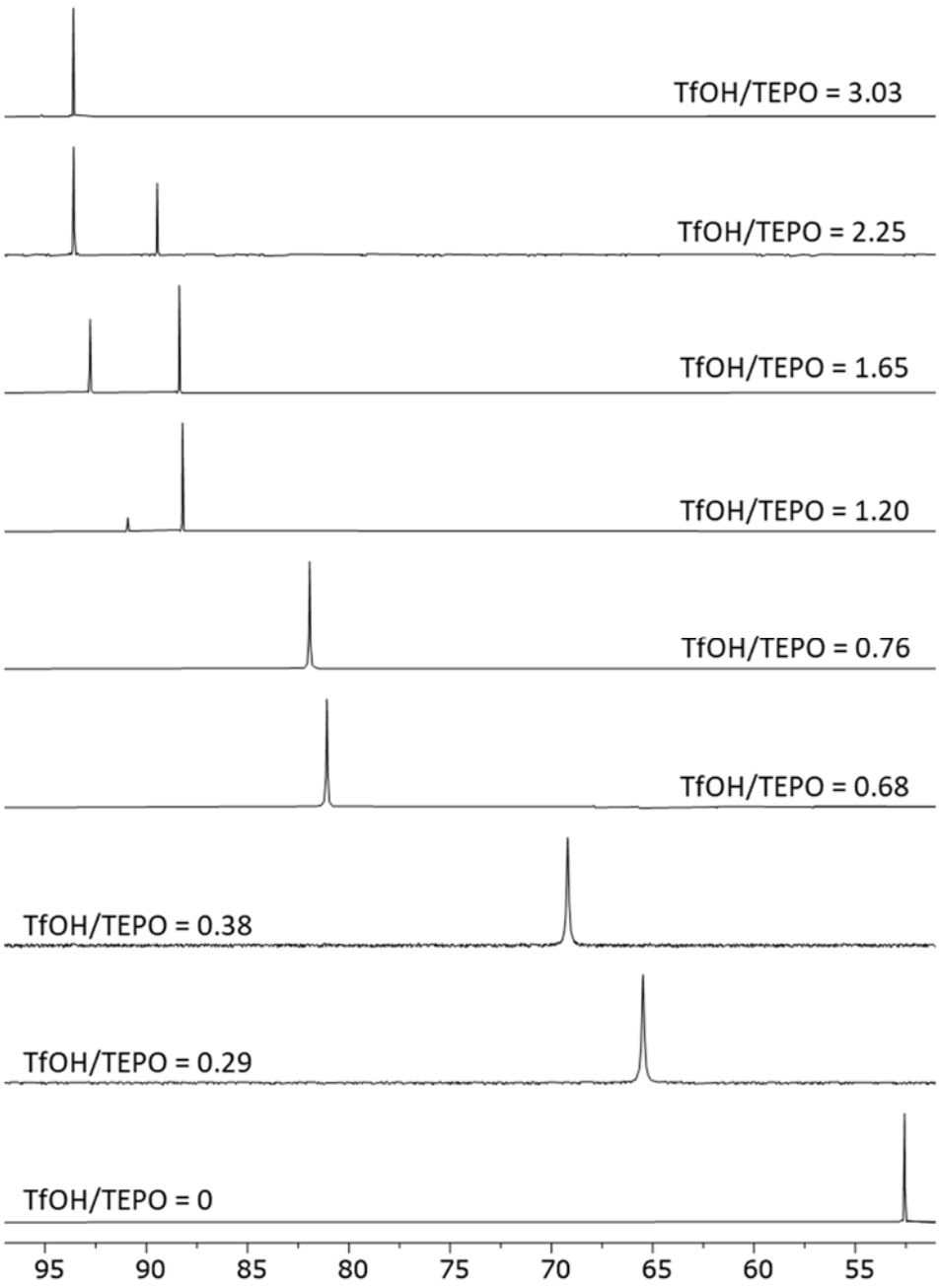


**Fig. S15.** Variation of $^{31}P$ chemical shift (ppm) with TfOH/TEPO molar ratio in $CDCl_3$.

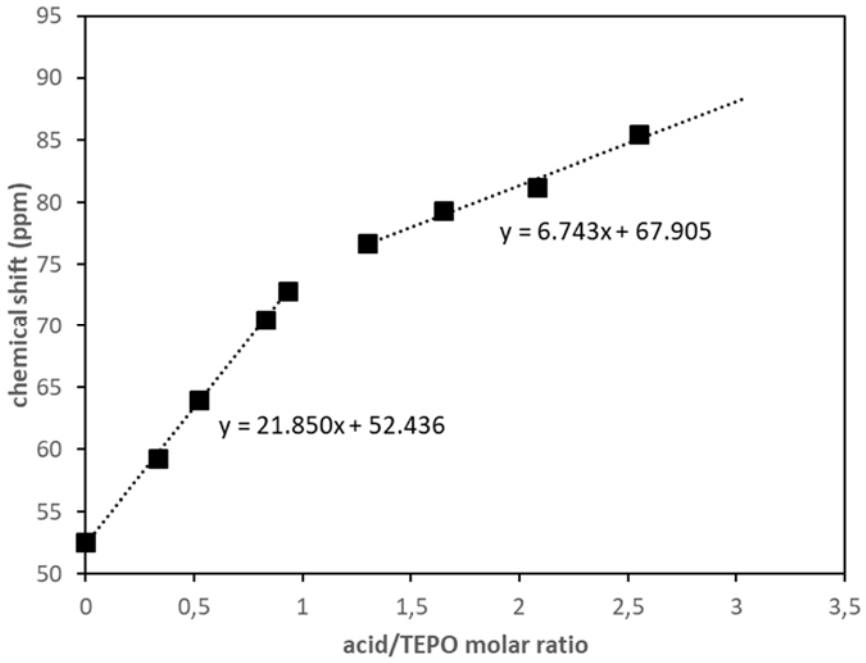


**Fig. S16.** Linear fits of $^{31}$P chemical shift (ppm) at low and high $MeSO_3H$/TEPO molar ratios.

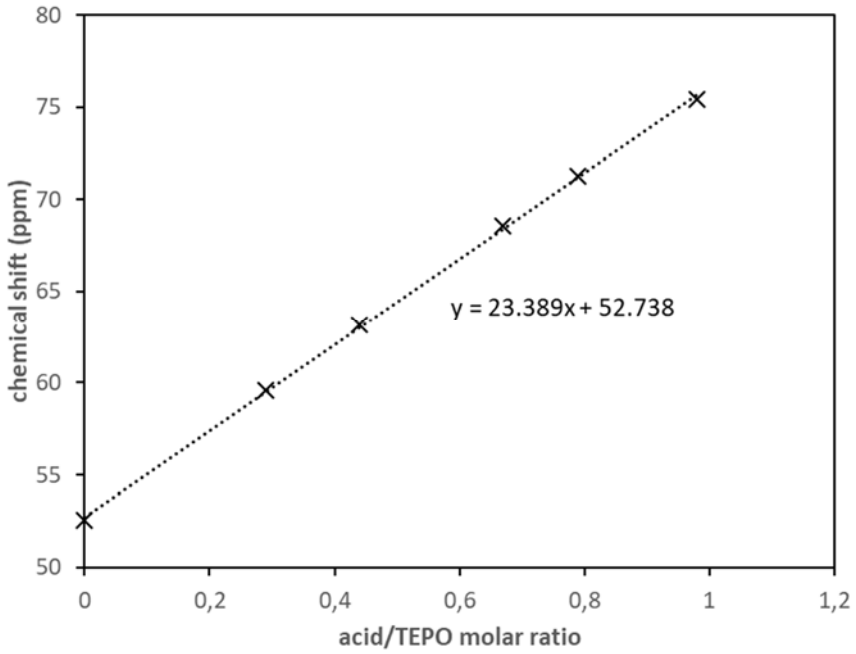


**Fig. S17.** Linear fit of $^{31}$P chemical shift (ppm) at low pTosH/TEPO molar ratio.

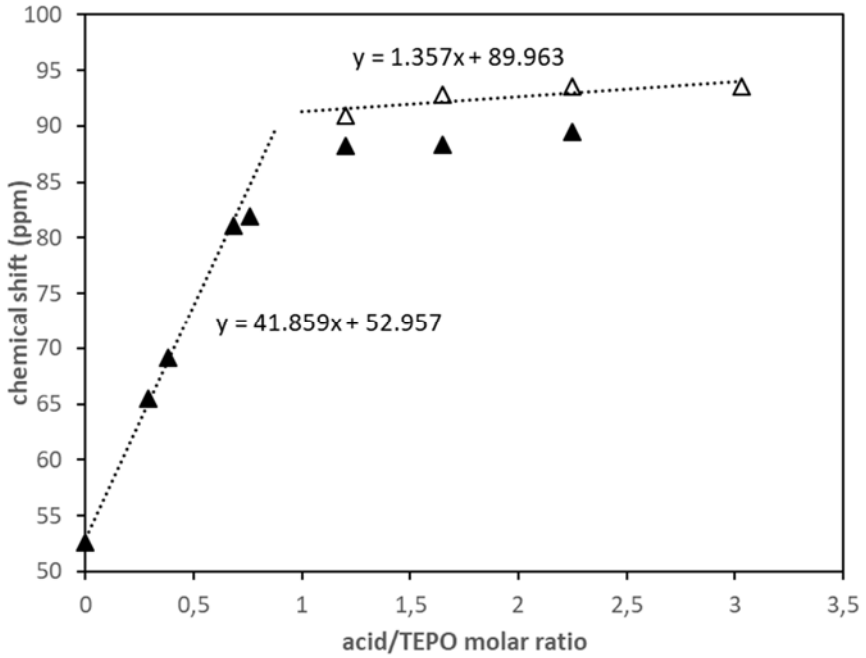


**Fig. S18.** Linear fits of $^{31}$P chemical shift (ppm) at low and high TfOH/TEPO molar ratios. Two signals appear at ratios > 1.

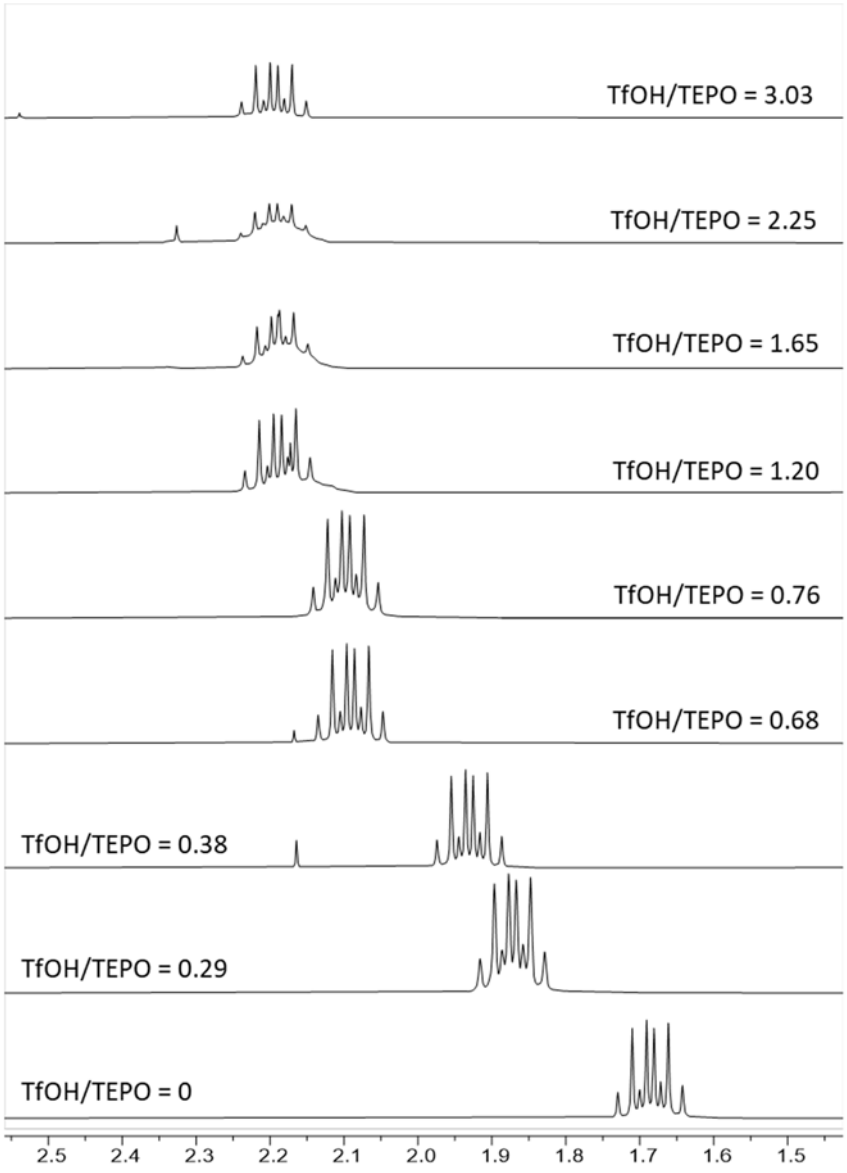


**Fig. S19.** Variation of $^{1}H$ chemical shift (ppm) of P-$CH_2$- groups with TfOH/TEPO molar ratio in $CDCl_3$.

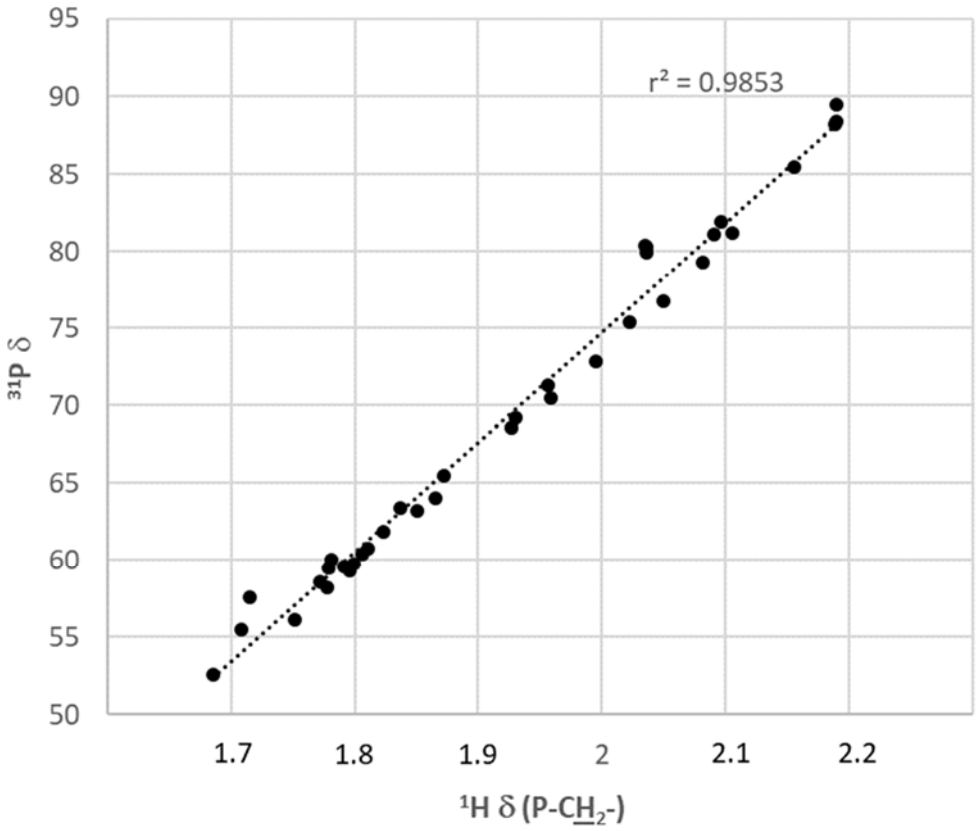


**Fig. S20.** Correlation between $^{31}P$ and $^{1}H$ (P-$CH_2$- signal) chemical shifts with all the acids and acid/TEPO molar ratios.

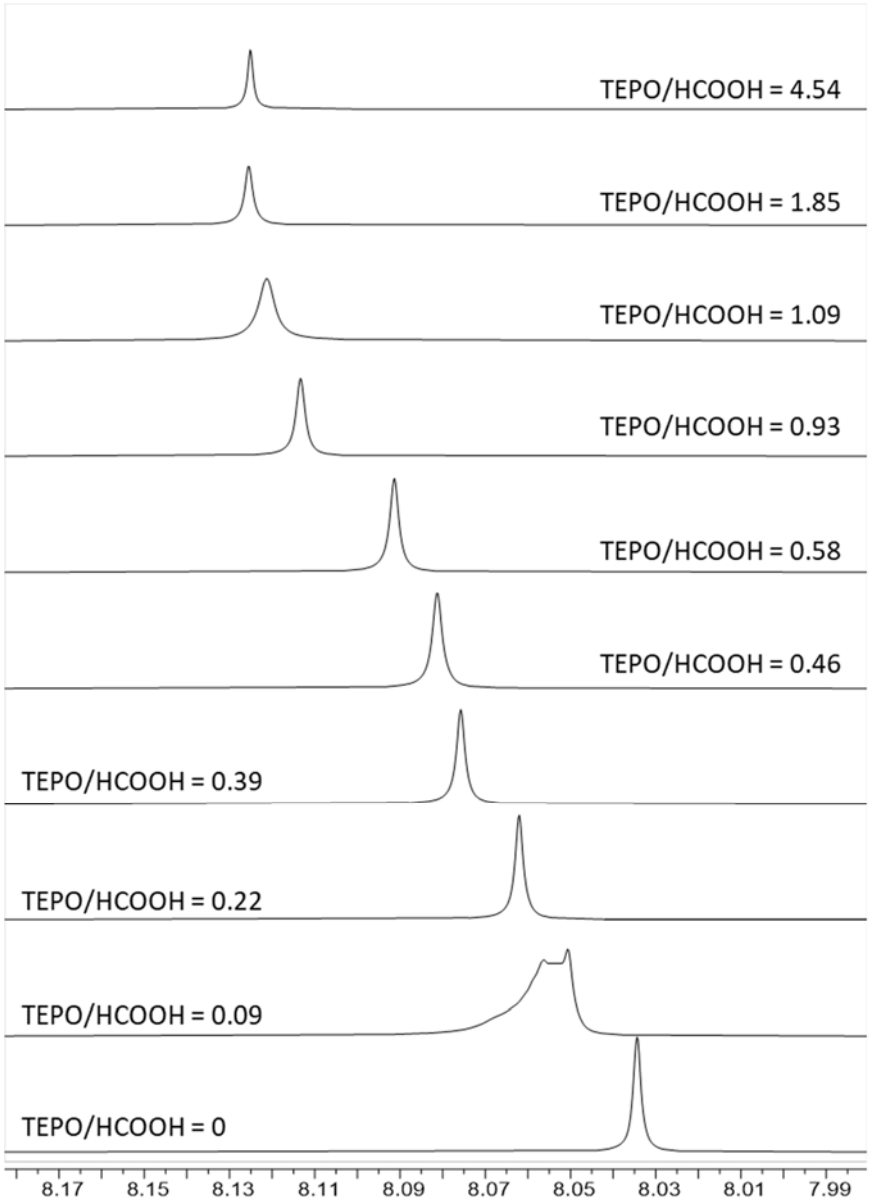


**Fig. S21.** Variation of $^{1}H$ chemical shift (ppm) of H-COOH with TEPO/HCOOH molar ratio in $CDCl_3$.

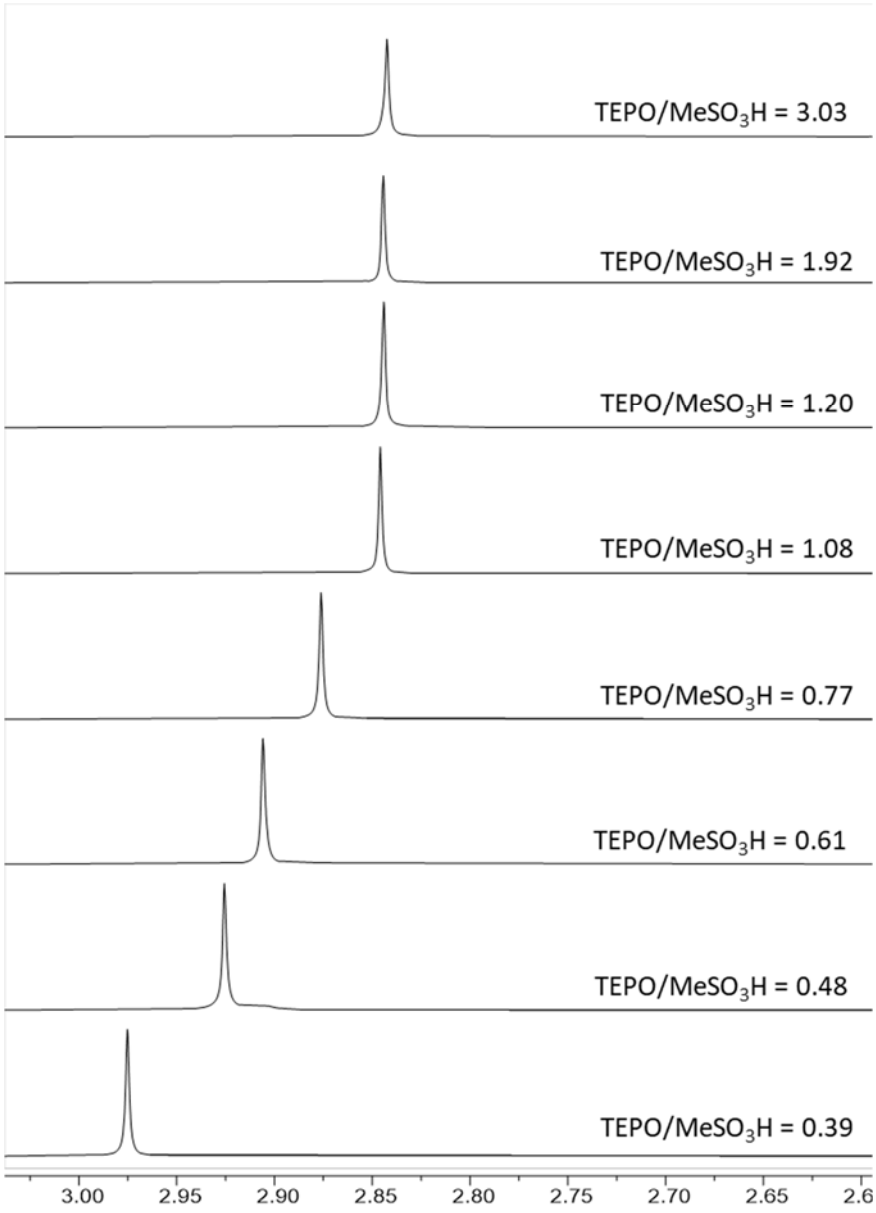


**Fig. S22.** Variation of $^{1}H$ chemical shift (ppm) of $C\underline{H_3}$-$SO_3H$ with $TEPO/MeSO_3H$ molar ratio in $CDCl_3$.

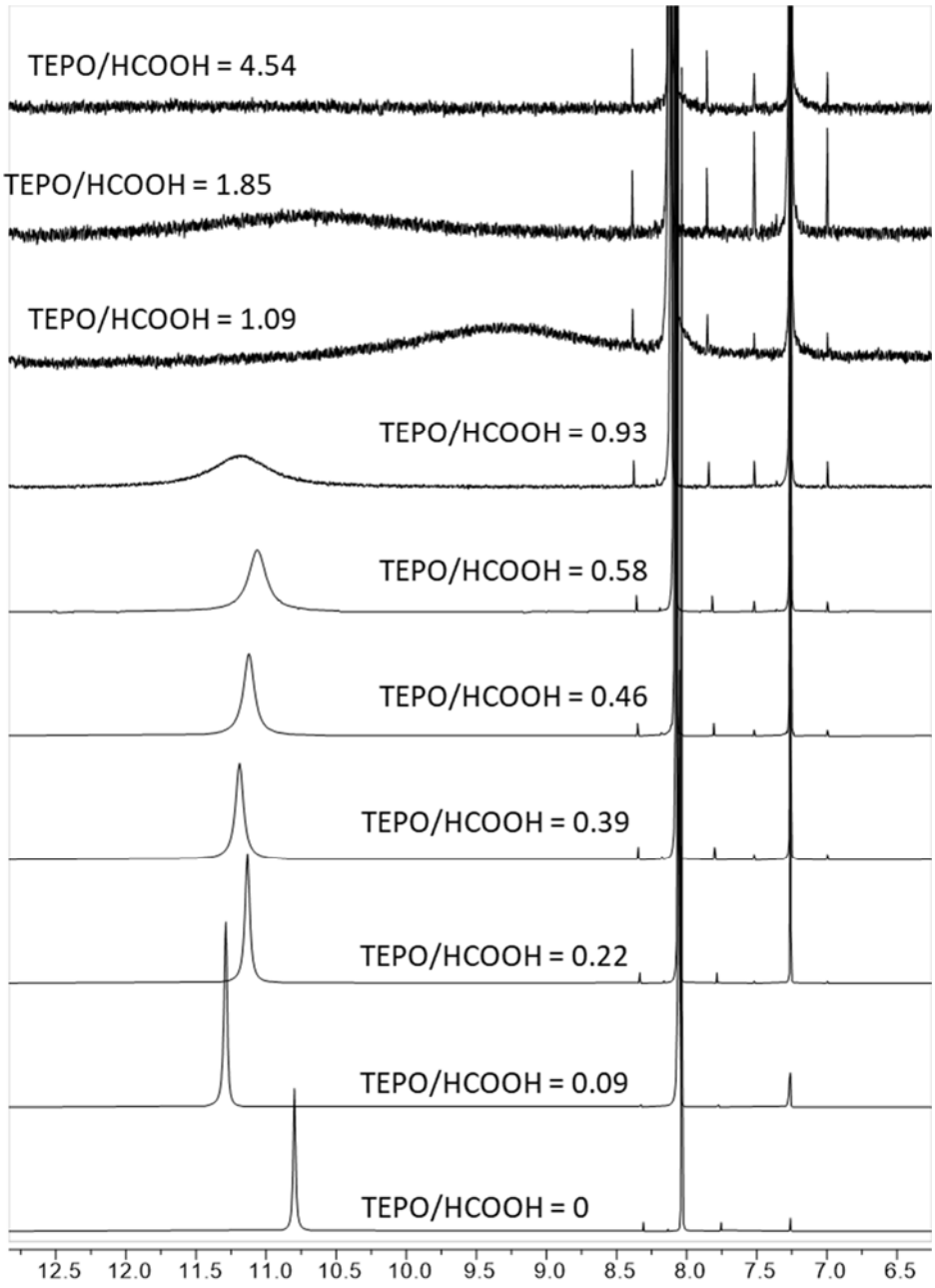


**Fig. S23.** Variation of $^{1}$H chemical shift (ppm) of H-COO<u>H</u> with TEPO/HCOOH molar ratio in $CDCl_3$.

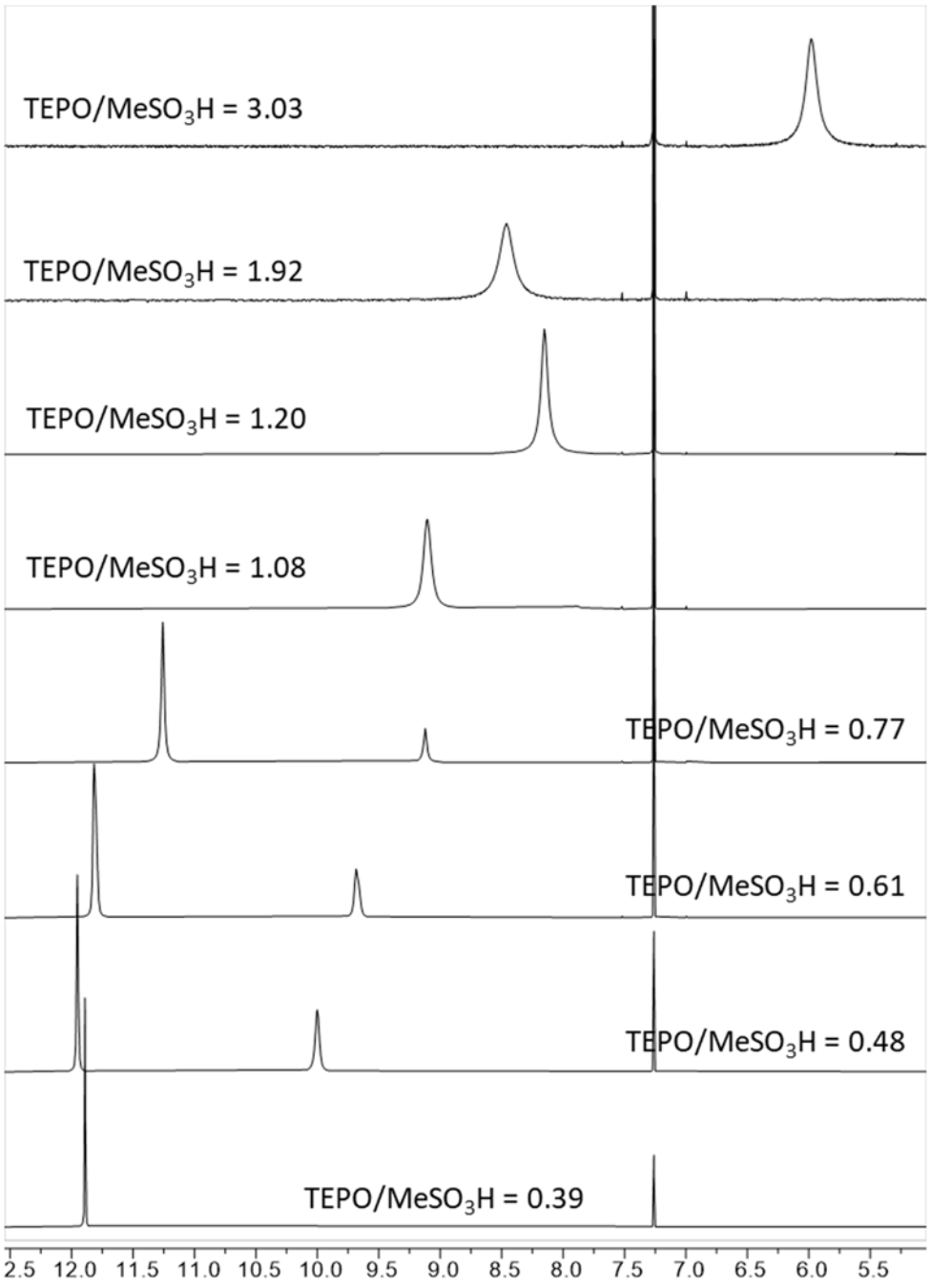


**Fig. S24.** Variation of $^{1}H$ chemical shift (ppm) of $CH_3$-$SO_3\underline{H}$ with TEPO/$MeSO_3H$ molar ratio in $CDCl_3$.

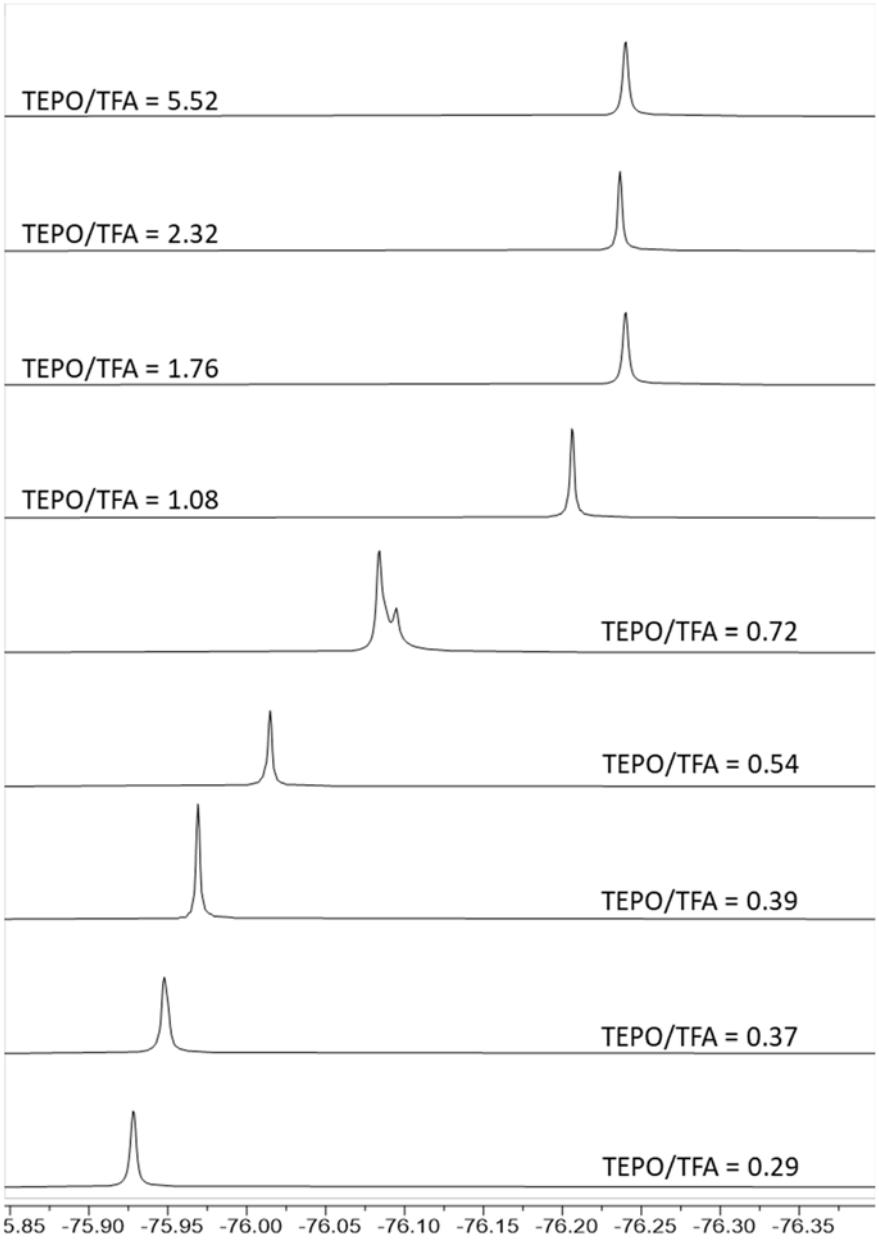


**Fig. S25.** Variation of $^{19}F$ chemical shift (ppm) of $C\underline{F_3}$-COOH with TEPO/TFA molar ratio in $CDCl_3$.

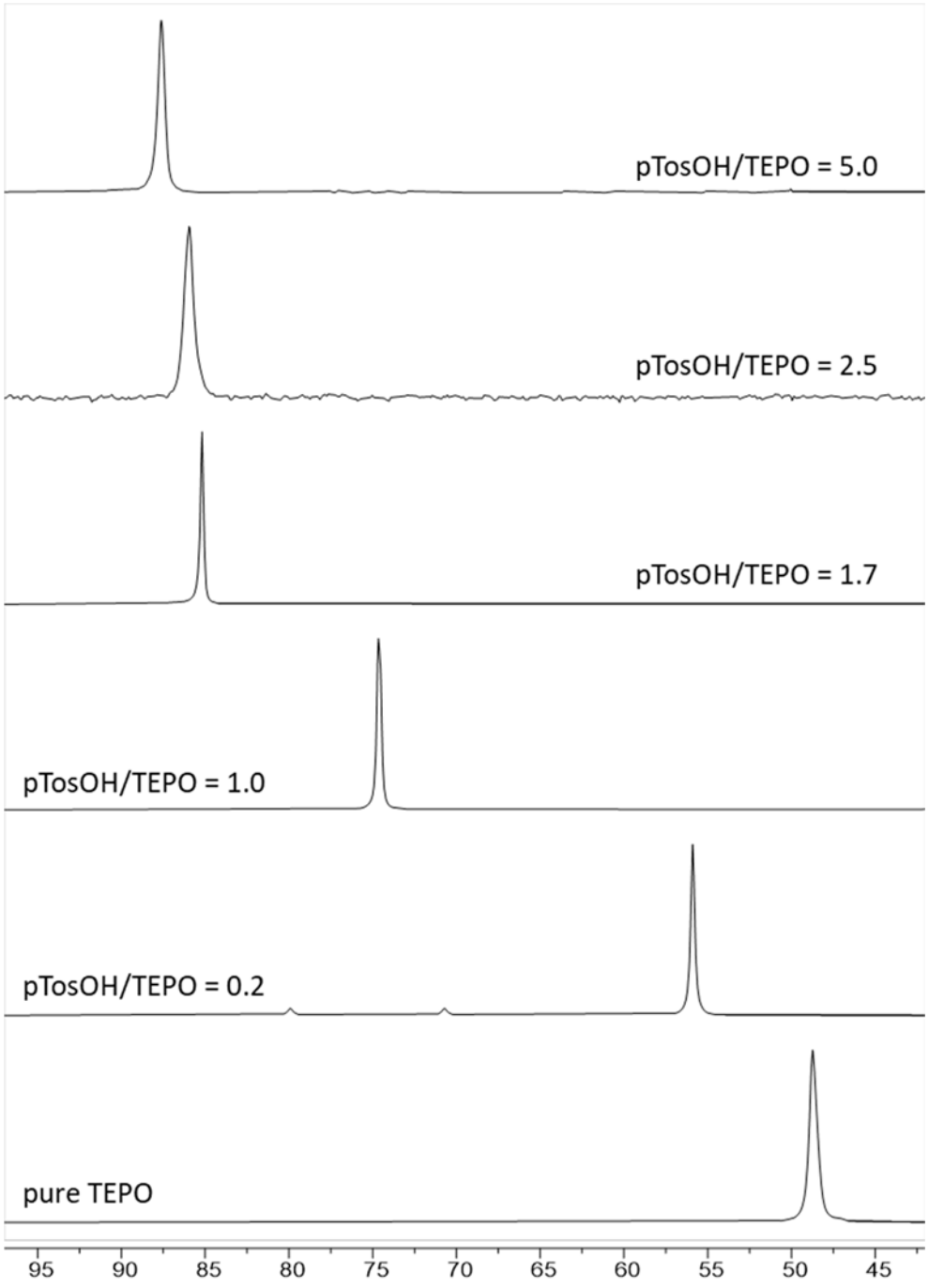


**Fig. S26.** Variation of $^{31}P$ chemical shift (ppm) with pTosOH/TEPO molar ratio in solid state (MAS-NMR). Liquid pTosOH-TEPO adducts were imbibed on solid KBr.

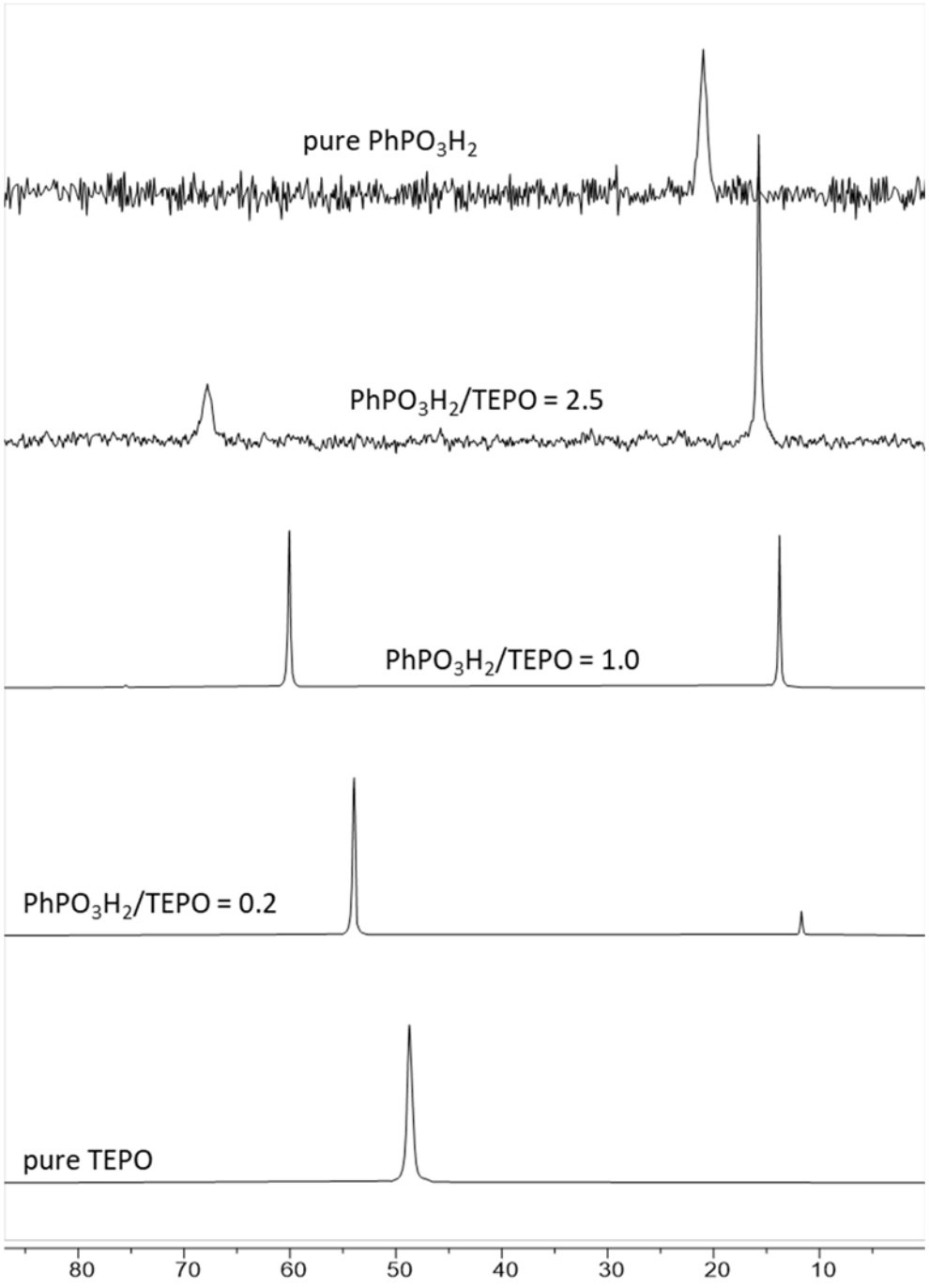


**Fig. S27.** Variation of $^{31}P$ chemical shift (ppm) with $PhPO_3H_2$/TEPO molar ratio in solid state (MAS-NMR). Liquid $PhPO_3H_2$-TEPO adducts were imbibed on solid KBr.

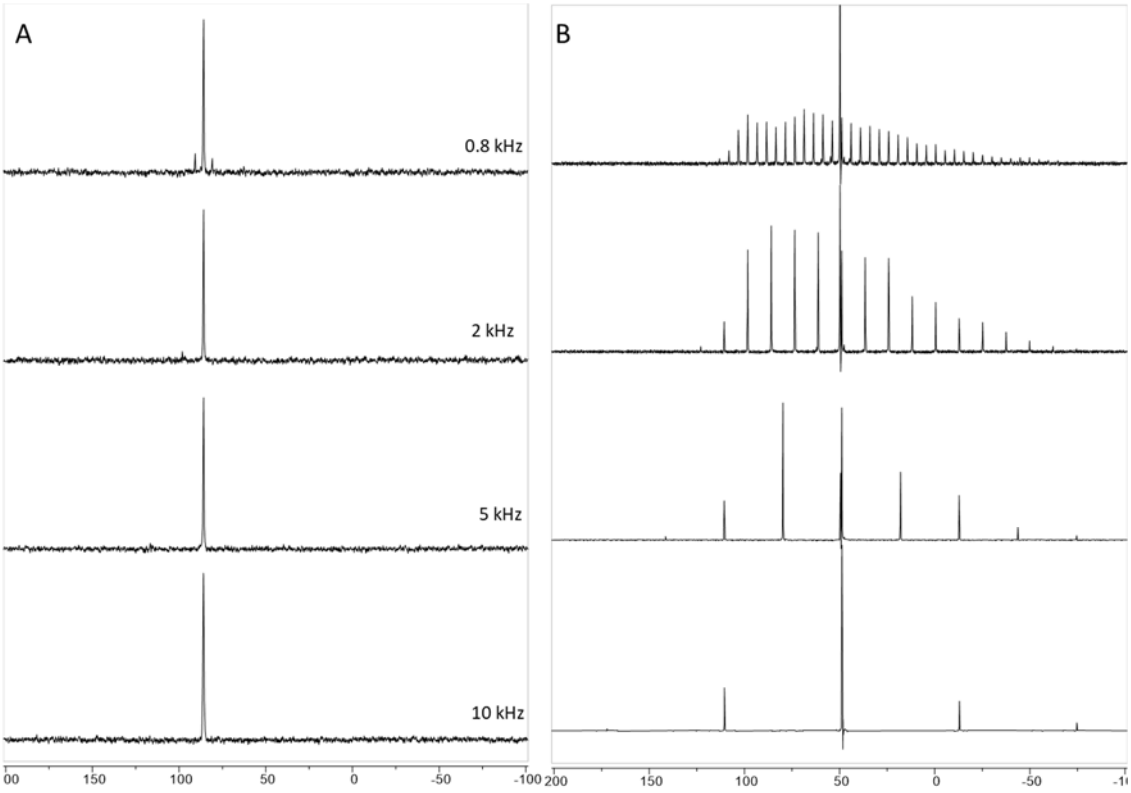


**Fig. S28**. Effect of spinning rate on the solid state (MAS NMR) spectra of: A) liquid pTosOH-TEPO adduct (acid/TEPO = 2.5) imbibed on solid KBr; B) pure TEPO.